THE EFFECT OF PREPARATION METHODS CONDITION ON THE ACTIVITY OF PALLADIUM AND PLATINUM CATALYSTS TOWARDS HYDROGENATION OF PALM OLEIN

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ABSTRACT

The hydrogenation of vegetable oils is an important practice in the modification of fats and oils especially to increase the stability of the oil. Highly unsaturated oil is susceptible to autoxidation, thermal decomposition and other reactions that affect the quality and flavor. Consequently, it is desired to partially hydrogenate the oil to improve shelf life. Another reason to hydrogenate vegetable oils is to improve its utility. The effect of ultrasonic irradiation (US) and microwave (MW) on the preparation of mono- and bimetallic Pd and Pt were compared with the conventional heating (CH) method. Besides that, their activities for the hydrogenation reaction of palm olein were also reported. The Pd, Pt and PdPt nanoparticles stabilized with polyvinylpyrrolidone (PVP) were prepared with molar ratio of PVP to metal of 40:1. Small size particles that are highly dispersed were obtained after 2, 10 and 40 min under MW for Pd, PdPt and Pt colloidal nanoparticles respectively. The average particles size for Pd, Pt and PdPt was 1.24, 1.03 and 1.05 nm respectively. Meanwhile US also enhanced the reduction process, where reduction process completed after 5, 30, and 60 min for Pd, Pt and PdPt nanoparticles. However, large particle sizes were obtained under ultrasonic irradiation. The Pd nanoparticles have bimodal distribution with average sizes of 1.37 and 2.68nm. The Pt and PdPt nanoparticles have only one distribution with average particles size of 1.42 and 1.28nm respectively. Whereas, CH method with takes 3 hours has produced Pd, Pt and PdPt with particles sizes of 0.99, 1.20 and 1.23nm. The XRD analysis has strengthen the TEM result obtained, where broad peak obtained described small particles produced. From the XRD data, particles sizes were also re-calculated by using the Scherer equation and compared with the TEM result. It has shown that, the particles sizes calculated using the Scherer equation are slightly higher than that of the TEM result. Based from the XPS analysis, surface compositions of Pd and Pt show that PdPt(CH) and PdPt(MW) catalyst were in core-shell structure, meanwhile PdPt(US) was in alloy formation. The hydrogenation reaction of palm olein was conducted under ambient temperature and pressure with the molar ratio of palm olein to catalyst of 25000:1. The result shows that Pd(CH), Pt(MW), and PdPt(MW) catalysts achieved higher linoleate conversion. The conversion of linoleate, elaidate selectivity and iodine values (IVs) are increased in order of Pt<PdPt<Pd. Elaidate selectivity for Pd, Pt, and for PdPt catalysts (included prepared under CH, MW, and US) were at range 52-56%, 3.5-8%, 4.4-13.4% respectively. The IVs for Pd nanoparticles are slightly decreased from 57 to range of 41-43 after 180 min reaction time. On the other hand, IVs for Pt and PdPt shows highly decreased from 57 to minimum values of to 38 and 39 respectively. The hydrogenation reaction under ultrasonic irradiation has enhanced the catalytic reactivity. Statistical analyses had proved that different types of catalyst, method of catalyst prepared and reaction conditions give a significant effect on the composition of linoleate, oleate, elaidate and stearate.

ABSTRAK

Penghidrogenan minyak sayuran adalah langkah penting dalam pengubahsuaian lemak dan minyak terutama sekali dalam meningkatkan kestabilan minyak tersebut. Minyak yang kaya dengan lemak tidak tepu terdedah kepada pengoksidaan secara automatik, penguraian termal and pelbagai tindak balas lain yang memberi kesan kepada kualiti dan rasa. Oleh yang demikian, ia adalah diperlukan untuk menghidrogenkan minyak secara separa untuk memperbaiki jangka hayatnya. Penyebab lain untuk menghidrogenan minyak sayuran adalah untuk memperbaiki penggunaannya. Kesan penyediaan mangkin secara penyinaran ultrasonik (US) dan gelombang mikro (MW) kepada penyediaan mono- dan dwi- Pd and Pt dibandingkan dengan kaedah pemanasan secara konvensional (CH). Di samping itu, aktiviti pemangkin untuk tindak balas hidrogenan minyak olein juga dilaporkan. Nanopartikel Pd, Pt dan PdPt distabilkan dengan polyvinylpyrrolidone (PVP) disediakan dengan nisbah molar PVP kepada logam 40:1. Saiz partikel yang kecil dan tersebar jauh telah didapati selepas 2, 10, dan 40 min di bawah gelombang mikro masing-masing untuk nanopartikel Pd, Pt dan PdPt. Purata saiz partikel untuk Pd, Pt dan PdPt masing-masing adalah 1.24, 1.03, dan 1.05 nm. Pada masa yang sama kaedah US juga dapat mempertingkatkan proses penurunan, di mana proses penurunan selesai selepas 5, 30, dan 60 minit untuk nanopartikel Pd, Pt dan PdPt. Walau bagaimanapun, saiz partikel yang besar ditemui melalui penyinaran ultrasonik. Nanopartikel Pd mempunyai taburan dwimod dengan purata saiz 1.37 dan 2.68nm. Nanopartikel Pt dan PdPt hanya mempunyai satu taburan dengan purata masing-masing 1.42 and 1.28nm. Manakala, kaedah CH mengambil masa 3 jam untuk menghasilkan nanopartikel Pd, Pt dan PdPt dengan saiz 0.99, 1.20, dan 1.23nm. Analisa XRD telah memperkukuhkan keputusan yang didapati dari TEM, di mana puncak yang lebar didapati menunjukkan penghasilan partikel-partikel kecil. Daripada data XRD, saiz partikel dikira sekali lagi dengan menggunakan persamaan Scherer dan dibandingkan dengan keputusan TEM. Hasil menunjukkan bahawa saiz partikel yang dikira menggunakan persamaan Scherer adalah sedikit tinggi berbanding dengan keputusan dari TEM. Berdasarkan analisa XPS, nisbah komposisi di permukaan Pd dan Pt telah menunjukkan bahawa PdPt(CH) dan PdPt(MW) berada dalam bentuk teras(Pt)-tempurung(Pd) manakala PdPt(US) berada dalam bentuk aloi. Tindak balas penghidrogenasi minyak olein dikendalikan pada suhu dan tekanan persekitaran dengan nisbah molar minyak olein kepada pemangkin adalah 25000:1. Keputusan menunjukkan bahawa pemangkin Pd(CH), Pt(MW), dan PdPt(MW) mencapai penukaran linoleate yang tinggi. Penukaran linoleate, selektiviti elaidate, dan nilai iodin (IVs) meningkat mengikut urutan Pt < PdPt < Pd. Selektiviti terhadap elaidat untuk mangkin Pd, Pt, dan PdPt (termasuk pemyediaan melalui CH, MW, dan US) masing-masing adalah dalam julat 52-56%, 3.5-8% 4.4-13.4%. IV untuk partikel Pd sedikit berkurang daripada 57 kepada julat 41-43 selepas 180 min masa tindak balas. Selain itu, IV untuk Pt dan PdPt menunjukkan pengurangkan yang banyak daripada 57 kepada nilai minimum di mana masing-masing 38 dan 39. Tindak balas penghidrogenan melalui penyinaran ultrasonik telah mempertingkatkan tindakbalas pemangkin. Analisa statistik telah membuktikan

jenis pemangkin yang berbeza, kaedah penyediaan pemangkin dan keadaan tindak balas memberikan kesan yang penting ke atas komposisi linoleat, oleat, elaidat, dan stearat.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

d	Spacing between the planes in the atomic lattice
L	Average particles size
n	An integer
R^2	Regression
β	Corresponds to the full width at half maximum (FWHM, in radian)
θ	Angle between the incident ray and the scattering planes
λ	Wavelength of incident wave
η^2	Eta squared

LIST OF ABBREVIATIONS

BE	Binding Energy
CH	Conventional heating
CS	Conventional stirring
FAME	Fatty acid methyl ester
GC-FID	Gas chromatography equipped with FID detector
GLM	General linear model
HDL	High density lipoprotein
IV	Iodine value
LDL	Low density lipoprotein
MW	Microwave
TEM	Transmission electron microscopy
US	Ultrasonic irradiation
UV-VIS	Ultraviolet visible spectrophotometer
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffractometer

CHAPTER 1

INTRODUCTION

1.1 Hydrogenation of palm oil

The hydrogenation of vegetable oils is an important practice in the modifications of fats and oils. More than 70% of total edible oils globally are vegetable oils. The hydrogenation process was patented in 1903 and first commercialized by Procter & Gamble Corporation (Fernández et al., 2009). It is desirable to selectively hydrogenate the polyunsaturated acids to the monounsaturated fatty acid (oleic acid). Smith and co worker (2007) have stated the benefit of oleic acid, it can decrease the risk of coronary heart disease by decreasing low density lipoprotein (LDL), which are responsible for the movement of cholesterol within bloodstream. Briefly, the hydrogenation process converts liquid oil to a solid or semisolid product by means of multi-phase catalytic reaction with hydrogen. There are two main reasons why hydrogenation is important. Firstly it increased the stability of the oil. Highly unsaturated oil is susceptible to autoxidation, thermal decomposition, and other reactions that affect the flavor. Consequently, it is desired to partially hydrogenate the oil to improve shelf life. The second reason is to improve its utility. For most products, such as shortening, margarines, or confectionery fats, the desired softening and melting characteristics correspond to oils that are partially hydrogenated. In addition, it provides distinctive flavor, crispness, creaminess, and plasticity to common foods (Jang et al., 2005).

Basically vegetable oils are composed of triglycerides, which are ester of glycerol and fatty acids. The most common fatty acid chains in vegetable oils include, but are not limited to the saturated palmitic and stearic acids and unsaturated oleic, linoleic, and linolenic. Figure 1.1 illustrates the basic structure of triglyceride molecule

and also the most common fatty acid chains in vegetable oils. These fatty acid chains are randomly distributed among the triglycerides.

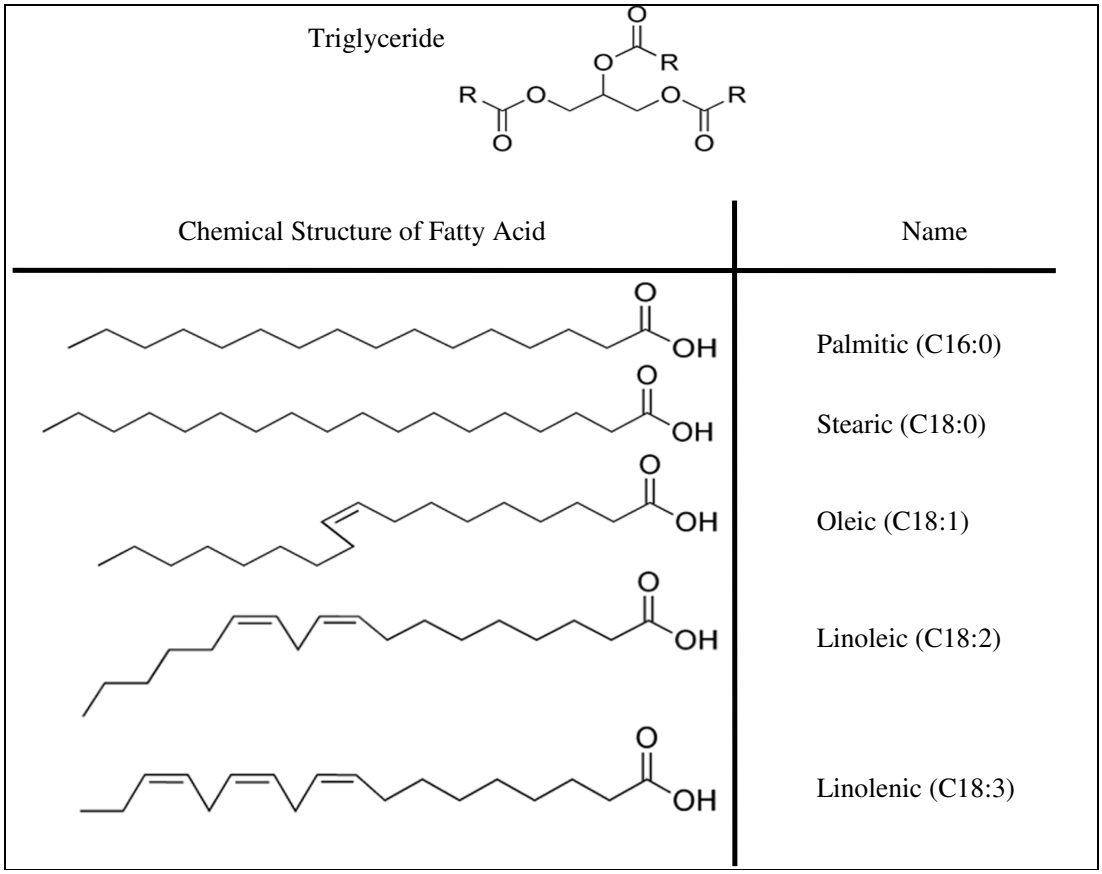


Figure 1.1: Basic structure of triglyceride and some of the most common fatty acid in vegetable oils

Industrial catalytic hydrogenation of palm olein with nickel (Ni) catalyst which is the liquid fraction of the semi-solid palm oil is to convert the trienes and dienes of the constituent fatty acids, respectively linolenic and linoleic, selectively to the monoenes, oleic or to saturated, stearic, for use in frying and baking applications (Izadifar et al., 2007; Simakova et al., 2008). However, during the hydrogenation, the monoenic acids originally present or formed as products may isomerizes from cis isomer to form trans isomer conformation (Deliy et al., 2009; Ribeiro et al., 2009). As the trans isomer are thermodynamically more stable they are invariably produced during hydrogenation. The trans-forms of the fatty acids are unhealthy for consumption (Fernández et al., 2009;

Guo et al., 2009) and their formation in edible fats during hydrogenation should be suppressed as far as possible. It is associated with an increased risk of cardiovascular disease by raising the level of serum low-density of lipoprotein (LDL) cholesterol and decreasing the level of high-density lipoprotein (HDL) cholesterol (Belkacemi et al., 2006).

1.2 Properties of noble metal catalyst

Application of metal nanoparticles in catalysis has attracted much attention because of their specific properties in chemistry and physics, which are distinctly different from those of bulk metal or single metal atom. Many researches focused on various metal nanoparticles have been published (Cano et al., 2011; Liu et al., 2010; Zhang et al., 2011; Zhou et al., 2010). The interest in synthetic routes that could generate new nano-structured materials has shown significant growth. For the noble metal colloids, the interest mainly focuses on catalytic applications. The choice of catalyst for hydrogenation reaction greatly affects the properties of edible oil.

The advantages of colloidally dispersed noble metal are precisely the advantages derived of colloidal particles in general; a large surface area; unique activities and spectroscopic features due to the size quantization of most electronic properties (Liu et al., 2010). For hydrogenation reaction many researches shows that nickel catalysts are not very active below 120°C. Noble metal catalysts are active event at ambient temperature (Choo et al., 2003; Jang et al., 2005). The hydrogenation reaction with noble metal catalyst does not require high temperature and pressure as required by conventional nickel hydrogenation. Besides that, hydrogenation at lower temperature and pressure can minimizes the isomerization of a cis isomer to trans isomer double bond conformation (Jang et al., 2005; Choo et al., 2001). As a result, formation of trans fatty acid also decreased.

Researches on noble metal nanoparticles are mainly on two aspects, preparation and application. Application of metal colloids in catalysis is an active research field (Fernández et al., 2009). It is known that the metal nanoparticles exhibit higher catalytic performance than conventional heterogeneous and homogeneous metal catalysts. Metal

nanoparticles have relatively high surface area and easy to agglomerate or aggregate. Thus, to find a suitable preparation method for small colloidal metal particles with narrow distribution is one of the essential prerequisites to obtain high performance nanoscopic metal catalysts.

1.3 Ultrasonic irradiation

Ultrasonic irradiation is now used widely for chemical synthesis at laboratory scale (Kumar et al., 2010). Many papers reported that ultrasonic irradiation effectively reduced the size of nanoparticles and accelerate reaction rate (Tu et al., 2008; Kumar et al., 2010). The use of sonochemistry in industry was initially hindered by the high cost associated with it. In recent years, it has started to attract attention because the cost may be off-set by reduction or elimination of other process costs. For example, the ultrasound enables reaction to take place at milder reaction condition (such as lower temperatures and pressures), and increase the activity of existing catalyst, accelerates the completion of reaction, hence increasing the desired product. For this reason, the use of ultrasound is a promising approach such as for producing high value chemicals, pharmaceuticals and synthesis of nanoparticles or nanocomposites. Researches in sonochemistry are continually expanding in many fields and are likely to make it a feasible option for large-scale processes.

1.4 Problem statement

Applications of noble metal catalysts gain much attention in recent decades. However, conventional heating technique required longer time to obtain colloidal metal nanoparticles. Thus, to find other method is crucial not only in order to increase the rate of reduction process but also to find a suitable preparation method for small colloidal metal particles with narrow particles size distribution is one of the essential prerequisites to obtaining nanoscopic metal catalysts with good catalytic performance (Yu et al., 2006).

One of the major tasks in catalysis research is tuning the selectivity in hydrocarbon conversion toward desirable reaction pathway. Particularly, controlling the

selectivity in the formation of cis and trans isomers has a significant practical importance for the production of cis unsaturated fatty acids during the partial hydrogenation of natural edible oil (Deliy et al., 2009; Ribeiro et al., 2009). Even though conventional catalytic studies and more modern surface-science work have provided much insight, detailed understanding of phenomena controlling cis-trans selectivity is still being researched.

1.5 Objectives and Scopes of work

The objectives of this research are to study the effect of preparation and reaction condition on the activity of palladium and platinum catalysts towards hydrogenation reaction of palm olein. A microwave and ultrasonic irradiation methods are selected to prepare the catalyst and in-comparison with the conventional heating method. The purpose is to elucidate the use of microwave and ultrasonic irradiation in synthesizing metal nanoparticles with small particles size and highly dispersed catalyst. Characterization of mono- and bimetallic Pd and Pt catalysts are done using UV-Visible spectrophotometer (UV-Vis), Transmission electron microscopy (TEM) and X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Other factors influencing the particle size are also explored. Next, all the catalysts are tested for hydrogenation reaction under conventional stirring and ultrasonic irradiation. Then, the partially hydrogenated palm olein composition is analyzed with GC-FID. Based on the GC analysis results of the conversion of linoleate, trans selectivity, iodine value and compositions of oleate and stearate of partially hydrogenated palm olein are calculated and analyzed. Finally, statistical analysis is performed in order to determine either types of metal, method of catalyst preparation, or reaction condition that give significant effect to the composition of linoleate, oleate, elaidate, and stearate in hydrogenated palm olein.

This research is limited to the following scope of work:

a) Preparation of mono- and bimetallic nanoparticles using Pd and Pt only.
b) and reaction at ambient condition

1.6 Thesis structure

Chapter one of this thesis provides the general information and background of the research. Chapter two reviews the literature related to the chemical reduction method and factors that influence the rate of reduction, the formation of metal nanoparticles and used of microwave and ultrasonic irradiation to synthesize nanoparticles. This chapter also presents the effect of ultrasonic irradiation on chemical reactivity. Besides that, the effect of Pd and Pt catalyst for hydrogenation reaction of vegetable oils are also reviewed.

Chapter three discusses experimental techniques used in this work. This chapter gives detail information on how mono- and bimetallic Pd and Pt catalysts are prepared in this research, and how the whole experiments are carried out. This chapter also provides the information about chemicals used and characterization procedures.

In chapter four, results of this work are presented and discussed. In specific, it discusses the effect of methods of reduction process and the effect of different catalyst on the composition of partially hydrogenated palm olein. Finally, chapter five consists of conclusion throughout the results and discussion of chapter 4 and ended with recommendations that can be used to improve further research.

CHAPTER 2

LITERATURE REVIEW

2.1 Synthesis of Metal Nanoparticles

The research and application on nanoparticles are influenced by the following five fundamental characteristics (Hoon, 2006).

- Metal core size, which will affect its optical and electronic properties
- Core size dispersion, which will influence the distribution of its properties
- Surface functionalization, which will stabilize and control its reactivity
- Stability, for ease of isolation, purification and storage
- Ease of synthesis

Particles are generally generated through nucleation and growth (Roucoux et al., 2002). Burda and co workers in 2005 concluded that particles growth could either be through primary or secondary growth. The primary growth refers to the growth of the particles size by molecular diffusion on the seed of the nuclei, whereas the secondary growth refers to collision and joining of two or more particles to form a new particle (Burda et al., 2005). The agglomerate and aggregate may resulted from the secondary growth process. Hoon (2006) stated that the difference between agglomerate and aggregate is in the binding energy of the nanoparticles. Agglomerate is a collection of two or more particles held together by a strong inter-particles force. In contrast, aggregate is described as particles that are held together by a weak cohesive force. Figure 2.1, shows the particles formation processes that have been described previously. Therefore, supporting or stabilizing agents are required to achieve well-dispersed small metal nanoparticles against agglomeration or aggregation.

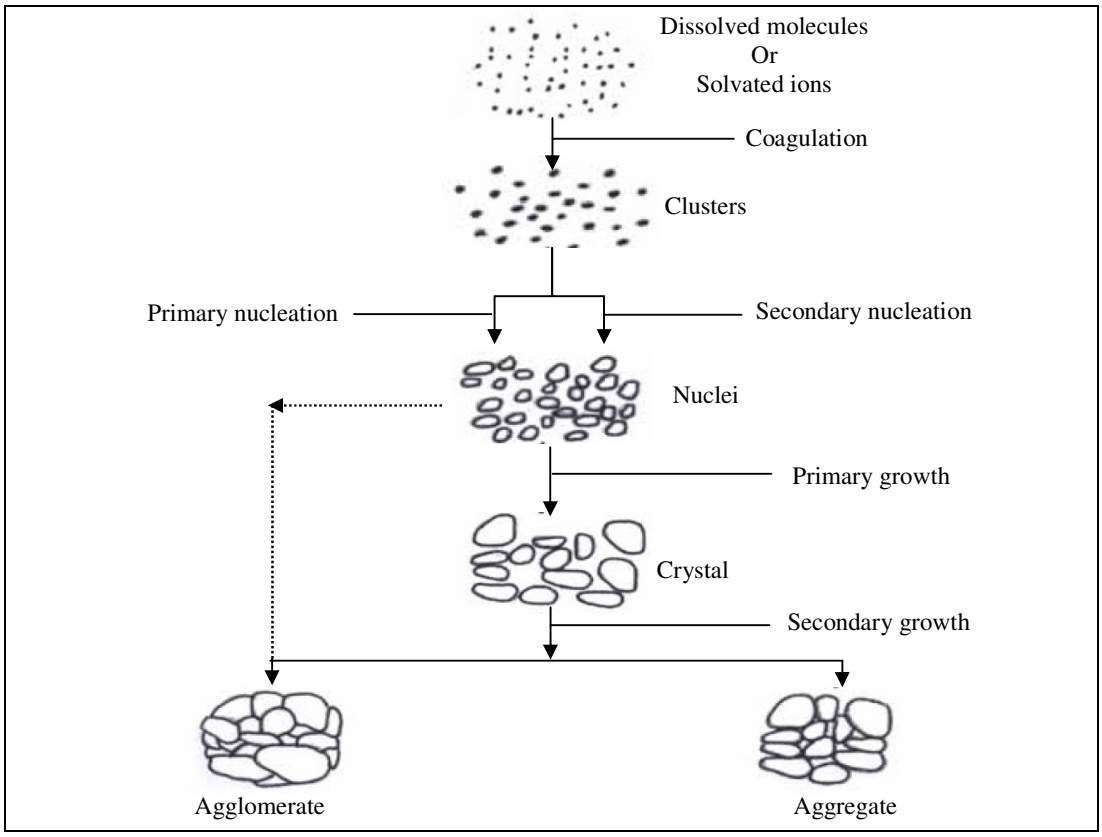


Figure 2.1: The schematic diagram of the particle formation in solution (Hoon, 2006)

2.2 Methods for metal nanoparticles preparation

Usually metal nanoparticles are synthesized by in-situ reduction method from a suitable metal precursor, such as through chemical reduction, photo-chemical reduction, electrochemical reduction and etc. For the chemical reduction method, a wide range of reducing agent has been used. Many reducing agents have been used to obtain colloidal nanoparticles such as alcohol (Evangelisti et al., 2010), sodium borohydride (Wani et al., 2011), sodium citrate (Roy et al., 2010). Further review on synthesizing metal nanoparticles via chemical reduction with alcohol will be done in detail in next subchapter.

2.2.1 Photo-chemical reduction

Photochemical synthesis of metal nanoparticles can be obtained either by (a) transitional metal salt reduction by radiolytically produced reducing agents or (b) degradation of an organometallic complex by radiolysis. The goal of these synthetic procedures is to obtain zero-valence metal under conditions which prevent the formation of aggregated metal nanoparticles. The ionization radiation is generated by X- or γ-ray generators while UV-visible irradiation is generated by the Hg or Xe lamp. One of the advantages of this method is that a large number of atoms are homogeneously and instantaneously produced during the irradiation thus providing favorable condition for the formation of nearly monodisperse particles (Roucoux et al., 2002). A wide range of metal nanoparticles especially Pt and Pd were prepared by this method since last two decades and the equations for the reactions are presented in the Figure 2.2 below. There are several reducing agents that can be generated during radiolytic procedure. The radiolysis of the aqueous suspension of metal salt produced solvated electron or $H^{\cdot}$ and $OH^{\cdot}$ originating from water radiolysis (Roucoux et al., 2002). These species can react with the molecules in the solution to give new radicals that are able to reduce metal salts.

Active species generation:

$$H_2O \longrightarrow H\cdot\ ,\ OH\cdot\ ,\ e^-\ ,\ H_3O^+\ ,\ H_2\ ,\ H_2O_2$$

$$OH\cdot(\ H\cdot) + RH \longrightarrow R^+ + H_2O(H_2)$$

Metal reduction:

$$M^{n+} + nR\cdot \longrightarrow M^0 + 2R\cdot + nH^+$$

$$M^{n+} + ne^- \longrightarrow M^0$$

Growth of colloids:

$$nM^0 \longrightarrow M^0_{colloid}$$

Figure 2.2: Radiolytic formation scheme of nanoparticles colloidal metal (Roucoux et al., 2002)

2.2.2 Electrochemical reduction

This method involves the use of a sacrificial anode as the metal source, which is oxidized in the presence of a quaternary ammonium salt, which acts as both the electrolyte and the stabilizer. The precursor metal ions are reduced at the cathode to yield the colloidal metal nanoparticles. This method has been successfully used to synthesize palladium, nickel, copper, platinum, rhodium, and ruthenium nanoparticles (Roucoux et al., 2002). An advantage to this method of synthesizing transition metal nanoparticles is that the particle size can be controlled by the current intensity. When the current intensity is increased, smaller transition metal nanoparticles are produced.

Reetz and co worker (1994) has developed an electrochemical method for the preparation of transition metal nanoparticles. This synthesis procedure allows one to obtain size-controlled particles. A sacrificial anode is used as a metal source and this anode is oxidized in the presence of quaternary ammonium salt, which serves as electrolyte and the stabilizing agent. Ions are reduced at the cathode to yield the metallic nanoparticles. Reetz and co-worker (1994) were able to generate acetonitrile/THF dispersed Pd colloids of various sizes. The mechanism proposed by the author, as illustrated in Fig 2.3 involves (a) dissolution of the anode to form metal ions (oxidation of Pd to Pd^{2+}); (b) migration of the metal ions to the cathode; (c) reduction of the metal ions at the surface of the cathode; (d) aggregation of the particles stabilized by the ammonium ions around the metal cores and (e) precipitation of the Pd nanoparticles.

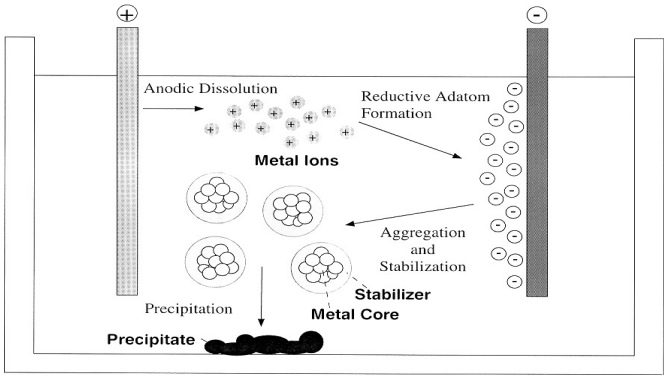
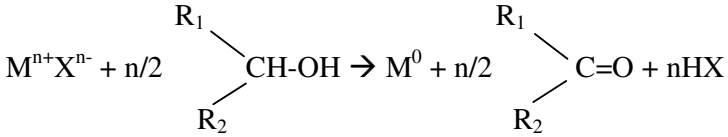


Figure 2.3: Reetz and co-workers' proposed mechanism for the formation of electrochemical synthesized metal colloids (Roucoux et al., 2002)

Reetz also found that there are several advantages of this process : (a) particles sizes can be controlled by varying the current intensity (higher current intensity gives smaller particle); (b) isolation of the nanoparticles is simple as they precipitate out of the solvent when formed and finally (c) the synthesis give good yields (>95%). This synthetic procedure can be applied to easily oxidized transition metals such as Ni and Cu. The solubility of the colloids obtained can be modulated from non-polar solvents such as pentane to polar solvents as water by changing the polarity of the protecting agent (tetraalkylammonium halide for apolar solvents or sulfobetaine for polar solvents). For less easily oxidized metals such as Pt, Rh, or Ru, the anode and cathode used are made of Pt and the metallic precursor is a transition metal salt.

2.3 Chemical reduction of metal ions by alcohol

Chemical reduction is one of the most widely used synthesis method to generate colloidal suspension of metals. This method is very simple and straightforward, and involved the reduction of metal salt with a reducing agent and the presence of stabilizer. A wide range of reducing agents have been used to obtain colloidal nanoparticles. In nanoparticles preparation process, alcohol can acts both as co-solvent and reducing agent for preparing nanoparticles. Generally, the alcohols which are useful reducing agent contained R-hydrogen. So, methanol, ethanol and 2-propanol are good reducing agent, while the *tert*-butyl alcohol is ineffective (Tu et al., 2008; Choo et al., 2006). During the reduction, the alcohols are oxidized to the corresponding carbonyl compound. Equation (2.1) shows the mechanism of metal salt reduction with alcohol.



$$M^{n+}X^{n-} + n/2 \begin{matrix} R_1 \\ \diagdown \\ CH\text{-}OH \\ \diagup \\ R_2 \end{matrix} \rightarrow M^0 + n/2 \begin{matrix} R_1 \\ \diagdown \\ C{=}O \\ \diagup \\ R_2 \end{matrix} + nHX \qquad (2.1)$$

Commonly used reducing agents included alcohol (Atobe et al., 2010; Lee et al., 2010), sodium borohydrate (Liu et al., 2010) and sodium citrate (Roy et al., 2010). Early 2011, Long and co worker successfully synthesized polyhedral morphology of PVP stabilized Pt nanoparticles. In this study, ethylene glycol (EG) was selected as reducing